

Theory of diatomic molecules in an external electromagnetic field from first quantum mechanical principles

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Abstract

We study a general problem of the translational/rotational/vibrational/electronic dynamics of a diatomic molecule exposed to an interaction with an arbitrary external electromagnetic field. The theory developed in this paper is relevant to a variety of specific applications. Such as, alignment or orientation of molecules by lasers, trapping of ultracold molecules in optical traps, molecular optics and interferometry, rovibrational spectroscopy of molecules in the presence of intense laser light, or generation of high order harmonics from molecules. Starting from the first quantum mechanical principles, we derive an appropriate molecular Hamiltonian suitable for description of the center of mass, rotational, vibrational and electronic molecular motions driven by the field within the electric dipole approximation. Consequently, the concept of the Born-Oppenheimer separation between the electronic and the nuclear degrees of freedom in the presence of an electromagnetic field is introduced. Special cases of the dc/ac field limits are then discussed separately. Finally, we consider a perturbative regime of a weak dc/ac field, and obtain simple analytic formulas for the associated Born-Oppenheimer translational/rotational/vibrational molecular Hamiltonian.

I. INTRODUCTION

During the last decade the manipulation of molecules by lasers has been extensively studied both theoretically and experimentally. The alignment and orientation of molecules by lasers have a large variety of applications in different fields of chemistry, physics, and potentially also in biology and material research [1]. Examples of recently demonstrated applications range from laser-assisted isotope separation [2] and catalysis [3], from pulse compression [4] and nanoscale design [5, 6] to tomographic imaging of molecules [7] and quantum information processing [8].

The Hamiltonian for molecules in an external electromagnetic field is of interest since it underlies a variety of phenomena associated with the electromagnetic field control of external and internal molecular motions, including trapping [9], molecular optics [5, 6, 10, 11, 12], Stark shift manipulation of the potential energy surfaces [13], and control of the high order harmonic generation [14].

Surprisingly, two qualitatively different forms of the rovibrational Hamiltonian for molecules in weak laser fields appear in the theoretical literature dealing with laser alignment. One form of the Hamiltonian has been derived in Ref. [15] and the other one in Ref. [16]. Both approaches, although being contradictory, have been used extensively in theoretical studies, giving thus rise to serious confusions and controversies. Most recently we have resolved this "puzzle" [17] by applying the adiabatic theorem for open systems using an extension of the (t, t') method, termed the (t, t', t'') approach [18].

The purpose of this work is to provide a detailed derivation of the Hamiltonian for diatomic molecules in laser fields, regardless if the involved field intensities are weak or strong. Our motivation is to analyze the most general case of a "diatomic molecule - electromagnetic field" interaction, such that the obtained results should be relevant not only for description of molecular alignment, but also for trapping of cold molecules in optical lattices, for rovibrational spectroscopy of molecules in the presence of intense laser light, or for generation of high order harmonics from molecules.

The paper is organized as follows. In Section II, we present a rigorous self contained derivation of an appropriate molecular Hamiltonian suitable for description of the center of mass, rotational, vibrational and electronic molecular motions driven by the field within the electric dipole approximation. Consequently, in Section III we introduce the framework of the Born-Oppenheimer separation between the electronic and the nuclear degrees of freedom in the presence of an electromagnetic field. Concept of a time dependent electronic potential energy surface is then discussed, with particular emphasis on the special cases of the dc/ac field limits. In Section IV, we consider a perturbative regime of a weak dc/ac field, and establish an interconnection between the corresponding Born-Oppenheimer electronic potential energy surfaces and the conventionally used static/dynamic molecular polarizabilities. Concluding remarks are given in Section V.

II. DIATOMIC MOLECULE IN AN ELECTROMAGNETIC FIELD: THE HAMILTONIAN

A. The Hamiltonian in momentum gauge and in laboratory frame coordinates

Let us study a diatomic molecule \mathcal{AB} exposed to an interaction with laser light. Some external electrostatic field can also be present. We prefer here to describe the considered electromagnetic field classically, in terms of the scalar potential $\phi(\vec{r}, t)$ and the vector potential $\vec{A}(\vec{r}, t)$, using Coulomb gauge and Gaussian units for the electromagnetic quantities [19]. The corresponding molecular Hamiltonian (expressed with respect to the laboratory space fixed coordinate frame) possesses an explicit form

$$\begin{aligned} \mathbf{H}(t) = & \frac{1}{2m_{\mathcal{A}}} \left[\vec{\mathbf{p}}_{\mathcal{A}} - \frac{Z_{\mathcal{A}}e}{c} \vec{A}(\vec{r}_{\mathcal{A}}, t) \right]^2 + \frac{1}{2m_{\mathcal{B}}} \left[\vec{\mathbf{p}}_{\mathcal{B}} - \frac{Z_{\mathcal{B}}e}{c} \vec{A}(\vec{r}_{\mathcal{B}}, t) \right]^2 + \frac{Z_{\mathcal{A}}Z_{\mathcal{B}}e^2}{|\vec{r}_{\mathcal{A}} - \vec{r}_{\mathcal{B}}|} \\ & + \sum_{j=1}^N \frac{1}{2m_e} \left[\vec{\mathbf{p}}_j + \frac{e}{c} \vec{A}(\vec{r}_j, t) \right]^2 + \sum_{j < j'} \frac{e^2}{|\vec{r}_j - \vec{r}_{j'}|} \\ & - \sum_{j=1}^N \frac{Z_{\mathcal{A}}e^2}{|\vec{r}_j - \vec{r}_{\mathcal{A}}|} - \sum_{j=1}^N \frac{Z_{\mathcal{B}}e^2}{|\vec{r}_j - \vec{r}_{\mathcal{B}}|} + Z_{\mathcal{A}}e\phi(\vec{r}_{\mathcal{A}}, t) + Z_{\mathcal{B}}e\phi(\vec{r}_{\mathcal{B}}, t) - e \sum_{j=1}^N \phi(\vec{r}_j, t) \quad . \quad (1) \end{aligned}$$

Here, symbol e stands for a charge of an electron, c denotes the velocity of light, $Z_{\mathcal{A}}$ and $Z_{\mathcal{B}}$ are the atomic numbers of the two nuclei \mathcal{A} and \mathcal{B} , while terms $m_{\mathcal{A}}, m_{\mathcal{B}}$ and m_e represent respectively the masses of nuclei \mathcal{A}, \mathcal{B} or the mass of an electron. An auxiliary index $j = 1, 2, \dots, N$ has been adopted for labelling the electronic variables. Other notations should be self explanatory.

B. The momentum gauge Hamiltonian in the center of mass and relative coordinates

As the first step of our derivation, we switch from the laboratory frame coordinates into the center of mass and relative coordinates. To accomplish this task, we introduce the center of mass position vector

$$\vec{R}_c = \frac{m_{\mathcal{A}}\vec{r}_{\mathcal{A}} + m_{\mathcal{B}}\vec{r}_{\mathcal{B}} + \sum_{j=1}^N m_e \vec{r}_j}{M} \quad ; \quad (2)$$

where the total mass

$$M = m_{\mathcal{A}} + m_{\mathcal{B}} + N m_e \quad . \quad (3)$$

In addition, we define the relative coordinates

$$\vec{R}_{\mathcal{AB}} = \vec{r}_{\mathcal{A}} - \vec{r}_{\mathcal{B}} \quad ; \quad (4)$$

and

$$\vec{q}_j = \vec{r}_j - \vec{R}_c \quad . \quad (5)$$

Relations inverse to the formulas (2), (4) and (5) are easily found to be

$$\vec{r}_{\mathcal{A}} = \vec{R}_c + \frac{m_{\mathcal{B}}}{m_{\mathcal{AB}}} \vec{R}_{\mathcal{AB}} - \frac{m_e}{m_{\mathcal{AB}}} \sum_{j=1}^N \vec{q}_j \quad ; \quad (6)$$

$$\vec{r}_{\mathcal{B}} = \vec{R}_c - \frac{m_{\mathcal{A}}}{m_{\mathcal{AB}}} \vec{R}_{\mathcal{AB}} - \frac{m_e}{m_{\mathcal{AB}}} \sum_{j=1}^N \vec{q}_j \quad ; \quad (7)$$

and

$$\vec{r}_j = \vec{R}_c + \vec{q}_j \quad . \quad (8)$$

An additional auxiliary symbol has been adopted here,

$$m_{\mathcal{AB}} = m_{\mathcal{A}} + m_{\mathcal{B}} \quad . \quad (9)$$

For the sake of completeness, we also mention in the present context that the volume element remains unchanged after the above described coordinate transformation, i.e.,

$$d^3 r_{\mathcal{A}} d^3 r_{\mathcal{B}} \prod_{j=1}^N d^3 r_j = d^3 R_c d^3 R_{\mathcal{AB}} \prod_{j=1}^N d^3 q_j \quad . \quad (10)$$

Proceeding further, we introduce the momenta associated with the new coordinates. Namely, we define the operators

$$\vec{\mathbf{P}}_c = -i\hbar \nabla_{\vec{R}_c} \quad , \quad \vec{\mathbf{P}}_{\mathcal{AB}} = -i\hbar \nabla_{\vec{R}_{\mathcal{AB}}} \quad , \quad \vec{\wp}_j = -i\hbar \nabla_{\vec{q}_j} \quad . \quad (11)$$

These new momenta are interconnected with the original laboratory frame momenta through the transformation formulas

$$\vec{\mathbf{p}}_{\mathcal{A}} = \frac{m_{\mathcal{A}}}{M} \vec{\mathbf{P}}_c + \vec{\mathbf{P}}_{\mathcal{AB}} - \frac{m_{\mathcal{A}}}{M} \sum_{j=1}^N \vec{\wp}_j \quad ; \quad (12)$$

$$\vec{\mathbf{p}}_{\mathcal{B}} = \frac{m_{\mathcal{B}}}{M} \vec{\mathbf{P}}_c - \vec{\mathbf{P}}_{\mathcal{AB}} - \frac{m_{\mathcal{B}}}{M} \sum_{j=1}^N \vec{\wp}_j \quad ; \quad (13)$$

and

$$\vec{\mathbf{p}}_j = \frac{m_e}{M} \vec{\mathbf{P}}_c + \vec{\wp}_j - \frac{m_e}{M} \sum_{j'=1}^N \vec{\wp}_{j'} \quad . \quad (14)$$

We continue by substituting Eqs. (2), (4), (5) and Eqs. (12), (13), (14) into Eq. (1). In order to simplify the obtained result, we employ the dipole approximation

$$\vec{A}(\vec{R}_c + \vec{\xi}, t) \approx \vec{A}(\vec{R}_c, t) \quad , \quad \phi(\vec{R}_c + \vec{\xi}, t) \approx \phi(\vec{R}_c, t) + \vec{\xi} \cdot \nabla_{\vec{R}_c} \phi(\vec{R}_c, t) \quad ; \quad (15)$$

which is justified as long as the spatial variation of the electromagnetic field remains negligible at the length scales $|\vec{\xi}|$ comparable to molecular dimensions. By using also the transversal property of the Coulomb gauge vector potential [19],

$$\nabla \cdot \vec{A}(\vec{r}, t) = 0 \quad ; \quad (16)$$

we write down an explicit expression for the Hamiltonian, Eq. (1), in the center of mass and relative coordinates. It holds

$$\begin{aligned}
\mathbf{H}(t) = & \frac{\vec{\mathbf{P}}_c^2}{2M} + \frac{\vec{\mathbf{P}}_{AB}^2}{2\mu_{AB}} + \sum_{j=1}^N \frac{\vec{\phi}_j^2}{2m_e} + \frac{Z_A Z_B e^2}{R_{AB}} + \sum_{j < j'} \frac{e^2}{|\vec{q}_j - \vec{q}_{j'}|} \\
& - \sum_{j=1}^N \frac{Z_A e^2}{\left| \vec{q}_j - (m_B/m_{AB}) \vec{R}_{AB} + (m_e/m_{AB}) \sum_{j'=1}^N \vec{q}_{j'} \right|} \\
& - \sum_{j=1}^N \frac{Z_B e^2}{\left| \vec{q}_j + (m_A/m_{AB}) \vec{R}_{AB} + (m_e/m_{AB}) \sum_{j'=1}^N \vec{q}_{j'} \right|} \\
& + \sum_{j=1}^N \frac{e}{c m_e} \vec{A}(\vec{R}_c, t) \cdot \vec{\phi}_j - \frac{e}{c} \left[\frac{Z_A}{m_A} - \frac{Z_B}{m_B} \right] \vec{A}(\vec{R}_c, t) \cdot \vec{\mathbf{P}}_{AB} \\
& - \frac{1}{2M} \sum_{jj'} \vec{\phi}_j \cdot \vec{\phi}_{j'} \\
& - \frac{(Z_A + Z_B - N)}{cM} \vec{A}(\vec{R}_c, t) \cdot \left[\vec{\mathbf{P}}_c - \sum_{j=1}^N \vec{\phi}_j \right] + e(Z_A + Z_B - N) \phi(\vec{R}_c, t) \\
& + e \left[(Z_A m_B - Z_B m_A)/m_{AB} \right] \vec{R}_{AB} \cdot \nabla_{\vec{R}_c} \phi(\vec{R}_c, t) - e \left[1 + (Z_A + Z_B)(m_e/m_{AB}) \right] \sum_{j=1}^N \vec{q}_j \cdot \nabla_{\vec{R}_c} \phi(\vec{R}_c, t) \\
& + \frac{e^2}{2c^2} \left[\frac{Z_A^2}{m_A} + \frac{Z_B^2}{m_B} + \frac{N}{m_e} \right] \vec{A}^2(\vec{R}_c, t) \quad .
\end{aligned} \tag{17}$$

In Eq. (17) an auxiliary shorthand symbol

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{18}$$

stands for the reduced mass of the AB molecule. Additional simplifications are in order: *i*) The term $(1/(2M)) \sum_{jj'} \vec{\phi}_j \cdot \vec{\phi}_{j'}$ in Eq. (17) can be neglected since the factor $(1/M)$ is small in magnitude. Similar argument applies also in the case of terms $(m_e/m_{AB}) \sum_{j=1}^N \vec{q}_j$. *ii*) For neutral molecules the $[Z_A + Z_B - N]$ -dependent contributions to Eq. (17) vanish. *iii*) The $\vec{A}^2(\vec{R}_c, t)$ factor can be eliminated from Eq. (17) by a trivial phase transformation [20], provided that we neglect additional corrections of the form $M^{-1}[\nabla_{\vec{R}_c} \int^t \vec{A}^2(\vec{R}_c, t') dt'] \cdot \vec{\mathbf{P}}_c$ and $M^{-1}[\Delta_{\vec{R}_c} \int^t \vec{A}^2(\vec{R}_c, t') dt']$ which arise due to non-commutativity between $\vec{A}(\vec{R}_c, t)$ and $\vec{\mathbf{P}}_c$. This step is justified as long as the spatial derivatives of the vector potential remain sufficiently small such that the translational motion of the molecule is not affected by the mentioned correction terms.

Having incorporated all the above simplifications, we rewrite the Hamiltonian (17) into a relatively simple functional form

$$\begin{aligned}
\mathbf{H}(t) = & \frac{\vec{\mathbf{P}}_c^2}{2M} + \frac{\vec{\mathbf{P}}_{AB}^2}{2\mu_{AB}} + \sum_{j=1}^N \frac{\vec{\phi}_j^2}{2m_e} + \frac{Z_A Z_B e^2}{R_{AB}} + \sum_{j < j'} \frac{e^2}{|\vec{q}_j - \vec{q}_{j'}|} \\
& - \sum_{j=1}^N \frac{Z_A e^2}{\left| \vec{q}_j - (m_B/m_{AB}) \vec{R}_{AB} \right|} - \sum_{j=1}^N \frac{Z_B e^2}{\left| \vec{q}_j + (m_A/m_{AB}) \vec{R}_{AB} \right|}
\end{aligned} \tag{19}$$

$$\begin{aligned}
& + \sum_{j=1}^N \frac{e}{c m_e} \vec{A}(\vec{R}_c, t) \cdot \vec{\wp}_j - \frac{e}{c} \left[\frac{Z_A}{m_A} - \frac{Z_B}{m_B} \right] \vec{A}(\vec{R}_c, t) \cdot \vec{P}_{AB} \\
& + e \left[(Z_A m_B - Z_B m_A) / m_{AB} \right] \vec{R}_{AB} \cdot \nabla_{\vec{R}_c} \phi(\vec{R}_c, t) - e \sum_{j=1}^N \vec{q}_j \cdot \nabla_{\vec{R}_c} \phi(\vec{R}_c, t) \quad .
\end{aligned}$$

The center of mass motion becomes here nonseparable from the internal molecular motions solely due to presence of the field terms $\vec{A}(\vec{R}_c, t)$ and $\phi(\vec{R}_c, t)$ in Eq. (19).

C. The length gauge Hamiltonian in the center of mass and relative coordinates

As the second step of our derivation, we convert the Hamiltonian (19) into the length gauge [20], which lends itself better for practical applications discussed later in Section III. The length gauge Hamiltonian $\bar{\mathbf{H}}(t)$ is obtained by an unitary transformation

$$\bar{\mathbf{H}}(t) = \mathbf{U}^\dagger(t) \mathbf{H}(t) \mathbf{U}(t) - i\hbar \mathbf{U}^\dagger(t) \frac{\partial}{\partial t} \mathbf{U}(t) \quad ; \quad (20)$$

with an unitary operator

$$\begin{aligned}
\mathbf{U}(t) = & \exp \left\{ -\frac{i}{\hbar} \frac{e}{c} \vec{A}(\vec{R}_c, t) \cdot \sum_{j=1}^N \vec{q}_j + \frac{i}{2m} \frac{Ne^2}{\hbar c^2} \int^t \vec{A}^2(\vec{R}_c, t') dt' \right\} \\
& \times \exp \left\{ i \frac{e \mu_{AB}}{\hbar c} \left[\frac{Z_A}{m_A} - \frac{Z_B}{m_B} \right] \vec{A}(\vec{R}_c, t) \cdot \vec{R}_{AB} + i \frac{e^2 \mu_{AB}}{2\hbar c^2} \left[\frac{Z_A}{m_A} - \frac{Z_B}{m_B} \right]^2 \int^t \vec{A}^2(\vec{R}_c, t') dt' \right\} .
\end{aligned} \quad (21)$$

Straightforward algebraic manipulations reveal that

$$\begin{aligned}
\bar{\mathbf{H}}(t) = & \frac{\vec{P}_c^2}{2M} + \frac{\vec{P}_{AB}^2}{2\mu_{AB}} + \sum_{j=1}^N \frac{\vec{\wp}_j^2}{2m_e} + \frac{Z_A Z_B e^2}{R_{AB}} + \sum_{j < j'} \frac{e^2}{|\vec{q}_j - \vec{q}_{j'}|} \\
& - \sum_{j=1}^N \frac{Z_A e^2}{\left| \vec{q}_j - (m_B/m_{AB}) \vec{R}_{AB} \right|} - \sum_{j=1}^N \frac{Z_B e^2}{\left| \vec{q}_j + (m_A/m_{AB}) \vec{R}_{AB} \right|} \\
& - \vec{D}_{AB}(\vec{R}_{AB}, \vec{q}^N) \cdot \left\{ \vec{E}^\parallel(\vec{R}_c, t) + \vec{E}^\perp(\vec{R}_c, t) \right\} \quad .
\end{aligned} \quad (22)$$

Here, the quantity

$$\vec{D}_{AB}(\vec{R}_{AB}, \vec{q}^N) = e \left[(Z_A m_B - Z_B m_A) / m_{AB} \right] \vec{R}_{AB} - e \sum_{j=1}^N \vec{q}_j \quad (23)$$

can be interpreted as the dipole moment operator of AB molecule, and symbols

$$\vec{E}^\perp(\vec{R}_c, t) = -\frac{1}{c} \frac{\partial \vec{A}(\vec{R}_c, t)}{\partial t} \quad , \quad \vec{E}^\parallel(\vec{R}_c, t) = -\nabla_{\vec{R}_c} \phi(\vec{R}_c, t) \quad (24)$$

stand for the transverse and the longitudinal electric fields assigned to the potentials $\vec{A}(\vec{R}_c, t)$ and $\phi(\vec{R}_c, t)$, respectively [19]. For the sake of completeness, we note by passing that in the formula (22) we have actually neglected additional corrections arising due to non-commutativity between

the operators $\vec{A}(\vec{R}_c, t)$ and $\Delta_{\vec{R}_c}$. Justification of this step is the same as in item *iii*) of the previous subsection II.B.

Before proceeding further in our derivation, let us mention a few interesting observations regarding the quantity (23). For homonuclear molecules ($m_A = m_B$ and $Z_A = Z_B$) the first term of equation (23) vanishes and thus only the electronic contribution $[-e \sum_{j=1}^N \vec{q}_j]$ is relevant. On the other hand, for cases where $Z_A = Z_B = Z$ but $m_A \neq m_B$ due to the use of different isotopes (such as HD for example), the formula (23) contains a factor $Ze [(m_B - m_A)/m_{AB}] \vec{R}_{AB}$ which is acting as a "permanent-like" dipole moment and influences the photo-induced molecular dynamics. The mentioned "permanent-like" dipole moment contribution arises in the case of isotopically substituted homonuclear molecules solely due to the fact that the nuclear center of mass is not located in the geometrical center of the \mathcal{A} – \mathcal{B} bond (which constitutes a molecular symmetry center from the point of view of electronic structure calculations). One might expect that the above discussed dipole moment component $e [(Z_A m_B - Z_B m_A)/m_{AB}] \vec{R}_{AB}$ becomes even more important in the case of heteronuclear diatomics ($m_A \neq m_B$ and $Z_A \neq Z_B$).

D. The length gauge Hamiltonian in the spherical polar coordinates

As the third step of our derivation, we replace the three cartesian coordinates $\vec{R}_{AB} = (X_{AB}, Y_{AB}, Z_{AB})$ by their spherical polar counterparts (R, ϑ, φ) . We employ the usual transformation procedure which is well known e.g. from standard textbook treatments of the hydrogen atom [21]. The corresponding transformation formula reads as

$$\begin{pmatrix} X_{AB} \\ Y_{AB} \\ Z_{AB} \end{pmatrix} = \mathcal{M}(\vartheta, \varphi) \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix} ; \quad (25)$$

where the rotation matrix

$$\begin{aligned} \mathcal{M}(\vartheta, \varphi) &= \begin{pmatrix} +\cos \varphi & -\sin \varphi & 0 \\ +\sin \varphi & +\cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} +\cos \vartheta & 0 & +\sin \vartheta \\ 0 & 1 & 0 \\ -\sin \vartheta & 0 & +\cos \vartheta \end{pmatrix} = \\ &= \begin{pmatrix} \cos \vartheta \cos \varphi & -\sin \varphi & \sin \vartheta \cos \varphi \\ \cos \vartheta \sin \varphi & +\cos \varphi & \sin \vartheta \sin \varphi \\ -\sin \vartheta & 0 & +\cos \vartheta \end{pmatrix} \end{aligned} \quad (26)$$

is orthogonal,

$$\mathcal{M} \mathcal{M}^T = \mathcal{M}^T \mathcal{M} = \mathcal{I} . \quad (27)$$

The associated volume element is of course $d^3 R_{AB} = R^2 dR \sin \vartheta d\vartheta d\varphi$. What remains to be done is to rewrite the Hamiltonian (22) into the new coordinates. An appropriate procedure for resolving

this task is well established, see e.g. Chapter IX of Ref. [21]. Therefore, we display here explicitly just the final result,

$$\begin{aligned} \overline{\mathbf{H}}(t) = & \frac{\vec{\mathbf{P}}_c^2}{2M} + \frac{\mathbf{P}_R^2}{2\mu_{AB}} + \frac{\vec{\mathbf{L}}_{\vartheta\varphi}^2}{2\mu_{AB}R^2} + \sum_{j=1}^N \frac{\vec{\varrho}_j^2}{2m_e} + \frac{Z_A Z_B e^2}{R} + \sum_{j < j'} \frac{e^2}{|\vec{q}_j - \vec{q}_{j'}|} \\ & - \sum_{j=1}^N \frac{Z_A e^2}{|\vec{q}_j - (m_B/m_{AB}) \mathcal{M}(\vartheta, \varphi) \vec{R}_{AB}^{BF}|} - \sum_{j=1}^N \frac{Z_B e^2}{|\vec{q}_j + (m_A/m_{AB}) \mathcal{M}(\vartheta, \varphi) \vec{R}_{AB}^{BF}|} \\ & - \vec{D}_{AB}(R, \vartheta, \varphi, \vec{q}^N) \cdot \left\{ \vec{E}^{\parallel}(\vec{R}_c, t) + \vec{E}^{\perp}(\vec{R}_c, t) \right\} . \end{aligned} \quad (28)$$

Here, the radial momentum operator is defined as

$$\mathbf{P}_R = -i\hbar \frac{1}{R} \frac{\partial}{\partial R} R \quad ; \quad (29)$$

the squared angular momentum operator is given by

$$\vec{\mathbf{L}}_{\vartheta\varphi}^2 = -\frac{\hbar^2}{\sin^2 \vartheta} \left[\sin \vartheta \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{\partial^2}{\partial \varphi^2} \right] \quad ; \quad (30)$$

and an additional auxiliary symbol

$$\vec{R}_{AB}^{BF} = [0, 0, R] \quad . \quad (31)$$

To avoid confusion, let us note explicitly that the dipole moment operator (23) is now expressed in the form

$$\vec{D}_{AB}(R, \vartheta, \varphi, \vec{q}^N) = e \left[(Z_A m_B - Z_B m_A)/m_{AB} \right] \mathcal{M}(\vartheta, \varphi) \vec{R}_{AB}^{BF} - e \sum_{j=1}^N \vec{q}_j \quad . \quad (32)$$

E. The length gauge Hamiltonian in the body fixed electronic coordinates

In this step of our derivation, we transform the position vectors of all the electrons into the body fixed frame. The origin O of the body fixed coordinate system is set to be the molecular center of mass. Note that this choice of the origin is a bit different from the choice adopted within the usual spectroscopic literature, where the nuclear center of mass is considered instead (see for example Ref. [22]). We prefer to use here an alternative less conventional assignment of the origin O since it makes our formulation more transparent and enables us to avoid introducing additional approximations.

The body fixed $\oplus o_z$ axis is, by definition, parallel (although not always coincidental) with the direction of \vec{R}_{AB} . The body fixed o_x and o_y axes are constrained by the requirement $\oplus o_x \times \oplus o_y = \oplus o_z$. Choice of o_x and o_y is, however, not unique: An arbitrary rotation around o_z leads to an equivalent pair of body fixed axes (o'_x, o'_y) which are equally suitable as (o_x, o_y) . Hence, an unambiguous definition of o_x and o_y must be fixed by convention. In order to achieve maximum simplicity, we prefer to employ such a particular convention that

$$\vec{q}_j = \mathcal{M}(\vartheta, \varphi) \vec{r}_j \quad ; \quad (33)$$

where $\vec{\mathbf{r}}_j$ are the body fixed coordinates of vector \vec{q}_j . Since the matrix $\mathcal{M}(\vartheta, \varphi)$ is orthogonal, the volume element remains unaffected, $d^3q_j = d^3\mathbf{r}_j$. Having introduced the body fixed electronic coordinates, we continue further and define the associated momenta,

$$\vec{\mathbf{p}}_j = -i\hbar \nabla_{\vec{\mathbf{r}}_j} \quad . \quad (34)$$

These new momenta are interconnected with their space fixed counterparts through the transformation formulas

$$\vec{\varphi}_j = \mathcal{M}(\vartheta, \varphi) \vec{\mathbf{p}}_j \quad . \quad (35)$$

It is straightforward to rewrite the Hamiltonian (28) into the body fixed coordinates. Taking advantage of the orthogonality property (27), we arrive towards the desired result

$$\begin{aligned} \overline{\mathbf{H}}(t) = & \frac{\vec{\mathbf{P}}_c^2}{2M} + \frac{\mathbf{P}_R^2}{2\mu_{AB}} + \frac{\vec{\mathbf{L}}_{\vartheta\varphi}^2}{2\mu_{AB}R^2} + \sum_{j=1}^N \frac{\vec{\mathbf{p}}_j^2}{2m_e} + \frac{Z_A Z_B e^2}{R} + \sum_{j < j'} \frac{e^2}{|\vec{\mathbf{r}}_j - \vec{\mathbf{r}}_{j'}|} \\ & - \sum_{j=1}^N \frac{Z_A e^2}{\sqrt{\mathbf{x}_j^2 + \mathbf{y}_j^2 + [\mathbf{z}_j - (m_B/m_{AB})R]^2}} - \sum_{j=1}^N \frac{Z_B e^2}{\sqrt{\mathbf{x}_j^2 + \mathbf{y}_j^2 + [\mathbf{z}_j + (m_A/m_{AB})R]^2}} \\ & - \left[\mathcal{M}(\vartheta, \varphi) \vec{D}_{AB}^{BF}(R, \vartheta, \varphi, \vec{\mathbf{r}}^N) \right] \cdot \left\{ \vec{E}^{\parallel}(\vec{R}_c, t) + \vec{E}^{\perp}(\vec{R}_c, t) \right\} \quad . \end{aligned} \quad (36)$$

Here, the quantity

$$\vec{D}_{AB}^{BF}(R, \vartheta, \varphi, \vec{\mathbf{r}}^N) = e \left[(Z_A m_B - Z_B m_A)/m_{AB} \right] \vec{R}_{AB}^{BF} - e \sum_{j=1}^N \vec{\mathbf{r}}_j \quad (37)$$

represents the body fixed counterpart of the dipole moment vector (23). Note that in formula (36) the translational and rovibrational kinetic energy operators are completely decoupled from the kinetic energy operators of the electrons. This holds true in particular also for the electronic and the nuclear angular momenta. (The electronic angular momenta are not displayed here explicitly and appear only after switching into the spherical or cylindrical electronic coordinates.)

F. Final form of the Hamiltonian for diatomic molecules in an electromagnetic field

Summarizing all the elaborations of Section II, we may conclude that the quantum dynamics of the considered molecule AB interacting with an external electromagnetic field $\vec{A}(\vec{r}, t)$ and $\phi(\vec{r}, t)$ is described by the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Xi(\vec{R}_c, R, \vartheta, \varphi, \vec{\mathbf{r}}^N, t) = \overline{\mathbf{H}}(t) \Xi(\vec{R}_c, R, \vartheta, \varphi, \vec{\mathbf{r}}^N, t) \quad ; \quad (38)$$

where $\Xi(\vec{R}_c, R, \vartheta, \varphi, \vec{\mathbf{r}}^N, t)$ is the associated translational/rotational/vibrational/electronic wavefunction, and the appropriate Hamiltonian $\overline{\mathbf{H}}(t)$ is given by expression (36). To avoid confusion, let us note in passing that the electron spin variables are suppressed in the notation of the present paper,

since they never enter explicitly into our considerations. Nevertheless, the presence of an electronic spin is of course fully respected within our treatment, as well as the antisymmetry of the electronic wavefunctions.

Before proceeding further, it is convenient to introduce an additional simplification, based upon the factorization

$$\Xi(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t) = R^{-1} \Psi(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t) \quad . \quad (39)$$

The purpose of this factorization is to eliminate redundant difficulties arising due to a complicated functional form of the radial momentum (29). We refer again to standard textbooks [21] for a more detailed discussion of this issue. One can easily show that the redefined wavefunction $\Psi(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t)$ satisfies the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t) = \tilde{\mathbf{H}}(t) \Psi(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t) \quad ; \quad (40)$$

with the Hamiltonian

$$\tilde{\mathbf{H}}(t) = -\frac{\hbar^2}{2M} \Delta_{\vec{R}_c} - \frac{\hbar^2}{2\mu_{AB}} \frac{\partial^2}{\partial R^2} + \frac{\vec{\mathbf{L}}_{\vartheta\varphi}^2}{2\mu_{AB} R^2} + \mathbf{H}_{\text{el}}(R) + \mathbf{W}_{\text{el}}(\vec{R}_c, R, \vartheta, \varphi, t) \quad . \quad (41)$$

Here, the field free electronic Hamiltonian

$$\begin{aligned} \mathbf{H}_{\text{el}}(R) = & \sum_{j=1}^N \frac{\vec{\mathbf{p}}_j^2}{2m_e} + \frac{Z_A Z_B e^2}{R} + \sum_{j < j'} \frac{e^2}{|\vec{\mathbf{r}}_j - \vec{\mathbf{r}}_{j'}|} \\ & - \sum_{j=1}^N \frac{Z_A e^2}{\sqrt{\mathbf{x}_j^2 + \mathbf{y}_j^2 + [\mathbf{z}_j - (m_B/m_{AB})R]^2}} - \sum_{j=1}^N \frac{Z_B e^2}{\sqrt{\mathbf{x}_j^2 + \mathbf{y}_j^2 + [\mathbf{z}_j + (m_A/m_{AB})R]^2}} \quad ; \quad (42) \end{aligned}$$

the " \mathcal{AB} molecule - field" interaction term

$$\mathbf{W}_{\text{el}}(\vec{R}_c, R, \vartheta, \varphi, t) = - \left[\mathcal{M}(\vartheta, \varphi) \vec{D}_{AB}^{BF}(R, \vartheta, \varphi, \vec{r}^N) \right] \cdot \vec{E}(\vec{R}_c, t) \quad ; \quad (43)$$

and an overall electric field

$$\vec{E}(\vec{R}_c, t) = \vec{E}^{\parallel}(\vec{R}_c, t) + \vec{E}^{\perp}(\vec{R}_c, t) \quad . \quad (44)$$

III. DIATOMIC MOLECULE IN AN ELECTROMAGNETIC FIELD: THE TIME-DEPENDENT BORN-OPPENHEIMER ELECTRONIC POTENTIAL ENERGY SURFACES

A. The time-dependent electronic wavefunctions

For isolated molecules, the well known concept of the Born-Oppenheimer/adiabatic separation between the electronic and the nuclear degrees of freedom proved to be extremely useful, as it gives

a lot of physical insight by distinguishing between the electronic and the rovibrational molecular states. The purpose of this Section is to extend the formulation of the Born-Oppenheimer approach on cases when a molecule is exposed to an interaction with an electromagnetic field. For simplicity, we shall consider here just a diatomic molecule \mathcal{AB} for which an appropriate Hamiltonian has been discussed at length in the previous Section II.

As the first step of our analysis, we formally construct the time dependent Born-Oppenheimer electronic basis set, defined by particular solutions of the electronic time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Phi_n(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) = \left[\mathbf{H}_{\text{el}}(R) + \mathbf{W}_{\text{el}}(\vec{R}_c, R, \vartheta, \varphi, t) \right] \Phi_n(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) \quad . \quad (45)$$

The corresponding initial condition is conveniently chosen to be

$$\Phi_n(\vec{r}^N, t_0; \vec{R}_c, R, \vartheta, \varphi) = \Phi_n^0(\vec{r}^N; R) \quad ; \quad (46)$$

where t_0 is an as yet arbitrary time instant, and function $\Phi_n^0(\vec{r}^N; R)$ represents a solution of a field free electronic eigenproblem

$$\mathbf{H}_{\text{el}}(R) \Phi_n^0(\vec{r}^N; R) = \mathcal{E}_n^0(R) \Phi_n^0(\vec{r}^N; R) \quad . \quad (47)$$

In order to simplify the underlying notation, we assume here that the electronic Hamiltonian $\mathbf{H}_{\text{el}}(R)$ possesses a discrete spectrum labelled by a single collective index n . Note, however, that the continuum part of the spectrum of $\mathbf{H}_{\text{el}}(R)$ can be implicitly included in this way as well, by taking advantage of the box quantization procedure. For the sake of clarity, let us also recall once again that the electron spin variables have been suppressed in above formulas, although they are implicitly accounted for.

The wavefunctions defined by Eq. (45) depend only parametrically on the nuclear coordinates $(\vec{R}_c, R, \vartheta, \varphi)$. For each fixed nuclear configuration $(\vec{R}_c, R, \vartheta, \varphi)$, the associated collection of electronic states $\{|\Phi_n(t)\rangle\}$ forms a complete orthonormal basis set covering an entire Hilbert space of the electronic variables. The orthonormality and closure properties are granted here for every time instant t , since the time evolution according to the Schrödinger equation, Eq. (45), is unitary, and since the field free electronic eigenfunctions (47) entering into the initial condition (46) constitute themselves a complete orthonormal electronic basis set.

We note by passing that although the above initial condition (46) can be in principle used in the most general context, it carries an especially physically illuminating interpretation in the case when

$$\vec{A}(\vec{R}_c, t) = \vec{0} \quad , \quad \phi(\vec{R}_c, t) = 0 \quad , \quad \mathbf{W}_{\text{el}}(\vec{R}_c, R, \vartheta, \varphi, t) = \mathbf{0} \quad (t \leq t_0) \quad ; \quad (48)$$

valid for all the possible molecular positions \vec{R}_c under study. If so, each stationary quantum state of the considered molecule can be (of course for $t \leq t_0$ and in the absence of avoided crossings) characterized within the framework of the conventional Born-Oppenheimer approximation, as a product

of a specific electronic state $|\Phi_n^0\rangle \exp[-(i/\hbar)\mathcal{E}_n^0(R)(t-t_0)]$ and an appropriate nuclear component. When the field is switched on at $t > t_0$, it is natural to expect that the relevant electronic state n remains relatively well defined, provided that its time evolution is understood in the sense of equation (45). This idea stands behind our formulation of the generalized time dependent Born-Oppenheimer separation scheme which is elaborated in the coming subsection.

B. Generalized Born-Oppenheimer theory for time dependent Hamiltonians

Following the spirit of the Born-Oppenheimer approach, we expand the total molecular wavefunction as

$$\Psi(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t) = \sum_n \chi_n(\vec{R}_c, R, \vartheta, \varphi, t) \Phi_n(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) \quad . \quad (49)$$

Substitution of an ansatz (49) into the time dependent Schrödinger equation (40) leads towards a set of coupled differential equations for the as yet unknown expansion coefficients χ_n . That is,

$$i\hbar \frac{\partial}{\partial t} \chi_n(\vec{R}_c, R, \vartheta, \varphi, t) = \sum_{n'} \mathbf{h}_{nn'}(t) \chi_{n'}(\vec{R}_c, R, \vartheta, \varphi, t) \quad ; \quad (50)$$

where the operator

$$\mathbf{h}_{nn'}(t) = \mathbf{h}_{nn'}^{(0)}(t) + \mathbf{h}_{nn'}^{(1)}(t) + \mathbf{h}_{nn'}^{(2)}(t) \quad (51)$$

is defined in terms of its components through the formulas

$$\mathbf{h}_{nn'}^{(0)}(t) = \delta_{nn'} \left[-\frac{\hbar^2}{2M} \Delta_{\vec{R}_c} - \frac{\hbar^2}{2\mu_{AB}} \frac{\partial^2}{\partial R^2} + \frac{\vec{L}_{\vartheta\varphi}^2}{2\mu_{AB} R^2} \right] \quad ; \quad (52)$$

$$\begin{aligned} \mathbf{h}_{nn'}^{(1)}(t) = & -\frac{\hbar^2}{M} \langle \Phi_n | \nabla_{\vec{R}_c} | \Phi_{n'} \rangle_{\vec{r}^N} \cdot \nabla_{\vec{R}_c} - \frac{\hbar^2}{\mu_{AB}} \langle \Phi_n | (\partial/\partial R) | \Phi_{n'} \rangle_{\vec{r}^N} \frac{\partial}{\partial R} \\ & - \frac{\hbar^2}{\mu_{AB} R^2} \langle \Phi_n | (\partial/\partial \vartheta) | \Phi_{n'} \rangle_{\vec{r}^N} \frac{\partial}{\partial \vartheta} - \frac{\hbar^2}{\mu_{AB} R^2 \sin^2 \vartheta} \langle \Phi_n | (\partial/\partial \varphi) | \Phi_{n'} \rangle_{\vec{r}^N} \frac{\partial}{\partial \varphi} \quad ; \end{aligned} \quad (53)$$

$$\begin{aligned} \mathbf{h}_{nn'}^{(2)}(t) = \langle \Phi_n | \mathbf{h}_{nn'}^{(2)}(t) | \Phi_{n'} \rangle_{\vec{r}^N} = & -\frac{\hbar^2}{2M} \langle \Phi_n | \Delta_{\vec{R}_c} | \Phi_{n'} \rangle_{\vec{r}^N} - \frac{\hbar^2}{2\mu_{AB}} \langle \Phi_n | (\partial^2/\partial R^2) | \Phi_{n'} \rangle_{\vec{r}^N} \\ & - \frac{\hbar^2}{2\mu_{AB} R^2} \langle \Phi_n | (\partial^2/\partial \vartheta^2) | \Phi_{n'} \rangle_{\vec{r}^N} - \frac{\hbar^2 \cos \vartheta}{2\mu_{AB} R^2 \sin \vartheta} \langle \Phi_n | (\partial/\partial \vartheta) | \Phi_{n'} \rangle_{\vec{r}^N} \\ & - \frac{\hbar^2}{2\mu_{AB} R^2 \sin^2 \vartheta} \langle \Phi_n | (\partial^2/\partial \varphi^2) | \Phi_{n'} \rangle_{\vec{r}^N} \quad . \end{aligned} \quad (54)$$

Here, for the sake of notational compactness, the matrix elements over the electronic wavefunctions have been expressed in a condensed fashion, such that e.g.

$$\langle \Phi_n | (\partial/\partial R) | \Phi_{n'} \rangle_{\vec{r}^N} \equiv \int d^3 \mathbf{r}^N \Phi_n^*(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) \frac{\partial}{\partial R} \Phi_{n'}(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) \quad ; \quad (55)$$

and similarly for the other quantities of this kind appearing in Eqs. (53)-(54).

Relations (49) and (50) are still exact, as they constitute just a different equivalent representation of the original problem (40). Now, let us introduce the generalized adiabatic approximation, based upon neglecting all the off-diagonal ($n \neq n'$) terms $\mathbf{h}_{nn'}^{(1)}(t)$ and $\mathbf{h}_{nn'}^{(2)}(t)$ of the Hamiltonian. If so, an index n (used for labelling single dynamical electronic basis vectors) becomes a good quantum number, and equations (49) and (50) are simplified into

$$\Psi^{\text{BO}}(\vec{R}_c, R, \vartheta, \varphi, \vec{r}^N, t) = \chi_n^{\text{BO}}(\vec{R}_c, R, \vartheta, \varphi, t) \Phi_n(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) \quad ; \quad (56)$$

and

$$i\hbar \frac{\partial}{\partial t} \chi_n^{\text{BO}}(\vec{R}_c, R, \vartheta, \varphi, t) = \mathbf{h}_{nn}(t) \chi_n^{\text{BO}}(\vec{R}_c, R, \vartheta, \varphi, t) \quad . \quad (57)$$

Before proceeding further, let us briefly touch a question regarding the justification of the above approximative step. In analogy to the conventional case of the time independent (field free) Born-Oppenheimer approximation, it seems reasonable to suggest the perturbation method as a well defined way how to establish a criterion of validity for an adiabatic ansatz (56). If so, one might speculate that the adiabatic approximation (56)-(57) breaks down in presence of "near-degeneracies" whose enhancement or suppression can be strongly influenced by an electromagnetic field. An explicit elaboration of the just sketched ideas seems relatively straightforward but lies beyond the scope of the present text.

C. Time dependent electronic potential energy surfaces: The general case

Equation (57) is naturally interpreted as an effective time dependent Schrödinger equation which governs the nuclear motions of the \mathcal{AB} molecule in a given dynamical electronic state n . It is convenient to carry out an additional transformation which converts the associated effective Hamiltonian $\mathbf{h}_{nn}(t)$ into a more standard functional form understandable as a sum of the kinetic and the potential energy operators. To accomplish the mentioned task, one needs to eliminate the Hamiltonian term $\mathbf{h}_{nn}^{(1)}(t)$ containing the first order derivatives with respect to the nuclear coordinates. An appropriate procedure for this is based upon making a factorization

$$\chi_n^{\text{BO}}(\vec{R}_c, R, \vartheta, \varphi, t) = e^{w_n(\vec{R}_c, R, \vartheta, \varphi, t)} \xi_n(\vec{R}_c, R, \vartheta, \varphi, t) \quad ; \quad (58)$$

where an exponential factor $w_n(\vec{R}_c, R, \vartheta, \varphi, t)$ is chosen to satisfy a system of the first order partial differential equations

$$\nabla_{\vec{R}_c} w_n(\vec{R}_c, R, \vartheta, \varphi, t) = -\langle \Phi_n | \nabla_{\vec{R}_c} | \Phi_n \rangle_{\vec{r}^N} \quad , \quad \partial w_n / \partial R = -\langle \Phi_n | (\partial / \partial R) | \Phi_n \rangle_{\vec{r}^N} \quad (59)$$

$$\partial w_n / \partial \vartheta = -\langle \Phi_n | (\partial / \partial \vartheta) | \Phi_n \rangle_{\vec{r}^N} \quad , \quad \partial w_n / \partial \varphi = -\langle \Phi_n | (\partial / \partial \varphi) | \Phi_n \rangle_{\vec{r}^N} \quad ; \quad (60)$$

valid at every time instant t .

The question on general solvability of Eqs. (59)-(60) is nontrivial and it is out of the scope of this paper to discuss it. We shall assume for now that the desired solution $w_n(\vec{R}_c, R, \vartheta, \varphi, t)$ exists and is unique up to a constant factor. This is of course the case of a field free problem, where the time dependent electronic wavefunctions depend only on R and not on the other nuclear coordinates $(\vec{R}_c, \vartheta, \varphi)$. We refer also to other important special cases discussed in subsequent subsections III.D and III.E, where an exact or at least a well defined approximative solution can be shown to exist. In this context one should note that, even if the set of Eqs. (59)-(60) turns out to be generally not solvable, an essential concept of the Born-Oppenheimer separation represented by Eqs. (56)-(57) remains unaffected. The only controversy persists here on whether or not one can formulate the general Born-Oppenheimer theory in terms of the electronic potential energy surfaces. If not, one has to use the above untransformed Born-Oppenheimer Hamiltonian $\mathbf{h}_{nn}(t)$ which contains first order derivatives with respect to the nuclear coordinates.

Having fixed the exponential factor $w_n(\vec{R}_c, R, \vartheta, \varphi, t)$ according to Eqs. (59)-(60), an equation of motion for the wavefunction component $\xi_n(\vec{R}_c, R, \vartheta, \varphi, t)$ is found to be

$$i\hbar \frac{\partial}{\partial t} \xi_n(\vec{R}_c, R, \vartheta, \varphi, t) = \mathbf{h}_n^{\text{eff}}(t) \xi_n(\vec{R}_c, R, \vartheta, \varphi, t) \quad ; \quad (61)$$

where an effective translational-rotational-vibrational Hamiltonian

$$\mathbf{h}_n^{\text{eff}}(t) = -\frac{\hbar^2}{2M} \Delta_{\vec{R}_c} - \frac{\hbar^2}{2\mu_{AB}} \frac{\partial^2}{\partial R^2} + \frac{\vec{\mathbf{L}}_{\vartheta\varphi}^2}{2\mu_{AB} R^2} + V_n(\vec{R}_c, R, \vartheta, \varphi, t) \quad (62)$$

can be, indeed, understood as the kinetic energy operator of the nuclei plus an electronic potential term. An explicit expression for the mentioned potential is

$$V_n(\vec{R}_c, R, \vartheta, \varphi, t) = -i\hbar \frac{\partial}{\partial t} w_n(\vec{R}_c, R, \vartheta, \varphi, t) + \tilde{V}_n(\vec{R}_c, R, \vartheta, \varphi, t) \quad ; \quad (63)$$

with the term

$$\begin{aligned} \tilde{V}_n(\vec{R}_c, R, \vartheta, \varphi, t) = & \left[\mathbf{h}_{nn}^{(0)}(t) + \mathbf{h}_{nn}^{(1)}(t) \right] w_n(\vec{R}_c, R, \vartheta, \varphi, t) + \mathbf{h}_{nn}^{(2)}(t) \\ & - \frac{\hbar^2}{2M} \left[\nabla_{\vec{R}_c} w_n \right]^2 - \frac{\hbar^2}{2\mu_{AB}} \left[\partial w_n / \partial R \right]^2 \\ & - \frac{\hbar^2}{2\mu_{AB} R^2} \left[\partial w_n / \partial \vartheta \right]^2 - \frac{\hbar^2}{2\mu_{AB} R^2 \sin^2 \vartheta} \left[\partial w_n / \partial \varphi \right]^2 \quad . \end{aligned} \quad (64)$$

As a matter of fact, the dominant contribution to $V_n(\vec{R}_c, R, \vartheta, \varphi, t)$ is given by the first part of above equation (63). Magnitude of the second term (64) can be generally considered to be small, due to presence of inverse mass factors M^{-1} and μ_{AB}^{-1} . Similarly as in the usual textbook treatments of the time independent Born-Oppenheimer separation [23], the correction (64) can be assigned to a

difference between the Born-Oppenheimer and the adiabatic approximations. We shall neglect the term (64) in our subsequent considerations, taking just

$$V_n(\vec{R}_c, R, \vartheta, \varphi, t) = -i\hbar \frac{\partial}{\partial t} w_n(\vec{R}_c, R, \vartheta, \varphi, t) \quad . \quad (65)$$

D. Electronic potential energy surfaces: The dc-field limit

Let us investigate now a special case when the electromagnetic field varies only very slowly in time. Such a situation is referred as the dc (direct current) limit, and is encountered whenever an external electrostatic field $\phi(\vec{r}, t)$ is turned on and off sufficiently slowly, while the central frequency ω_L of the laser pulse $\vec{A}(\vec{r}, t)$ acquires a sufficiently small value (small with respect to the characteristic timescale of the electronic motions - i.e. practically even for microwaves). Theoretical analysis of this problem is facilitated by introducing a switching parameter $\eta(t)$ which modulates the slow field variations according to a formal prescription

$$\vec{E}(\vec{r}, t) = \vec{E}_{\text{dc}}(\vec{r}, \eta(t)) \quad , \quad d\eta(t)/dt \rightarrow 0 \quad . \quad (66)$$

For the sake of clarity, we quote in this context a simple example of a low (microwave) frequency CW light $\vec{E}(\vec{r}, t) = \vec{E}_0 \cos(\omega_L t - \vec{k}_L \cdot \vec{r})$ with $|\vec{k}_L| = \omega_L/c$ and $\vec{E}_0 \cdot \vec{k}_L = 0$. Here the switching parameter $\eta(t)$ can be defined just as $\omega_L t$ and is then interpreted as an indicator of an instantaneous value of the electric field strength.

Taking into account the property (66) of the field, it is clear that also the Hamiltonian interaction term (43) depends on time only through $\eta(t)$, and can be thus denoted by an extra symbol

$$\mathbf{W}_{\text{el}}^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta(t)) \equiv \mathbf{W}_{\text{el}}(\vec{R}_c, R, \vartheta, \varphi, t) = - \left[\mathcal{M}(\vartheta, \varphi) \vec{D}_{\text{AB}}^{\text{BF}}(R, \vartheta, \varphi, \vec{r}^N) \right] \cdot \vec{E}_{\text{dc}}(\vec{R}_c, \eta(t)) \quad . \quad (67)$$

If so, the dynamical electronic states (45) take an explicit functional form predicted by the well known adiabatic theorem [21]. It holds

$$\Phi_n(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) = \exp \left[-\frac{i}{\hbar} \int_{t_0}^t \mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau \right] \Phi_n^{\text{ad}}(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta(t)) \quad ; \quad (68)$$

where the η -adiabatic electronic energies and wavefunctions are defined by an eigenvalue problem

$$\left[\mathbf{H}_{\text{el}}(R) + \mathbf{W}_{\text{el}}^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta) \right] \Phi_n^{\text{ad}}(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta) = \mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta) \Phi_n^{\text{ad}}(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta) \quad . \quad (69)$$

Since the electronic Hamiltonian of equation (69) is real, the associated η -adiabatic electronic eigenstates $\Phi_n^{\text{ad}}(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta)$ can be also considered as real quantities. Therefore, the matrix element

$$\langle \Phi_n^{\text{ad}} | (\partial/\partial R) | \Phi_n^{\text{ad}} \rangle_{\vec{r}^N} = 0 \quad ; \quad (70)$$

and, consequently,

$$\langle \Phi_n | (\partial/\partial R) | \Phi_n \rangle_{\vec{r}^N} = -\frac{i}{\hbar} \frac{\partial}{\partial R} \int_{t_0}^t \mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau \quad . \quad (71)$$

Analogical relations are valid also for the other matrix elements appearing on right hand sides of Eqs. (59)-(60). This shows that an appropriate solution of the problem (59)-(60) possesses the form

$$w_n(\vec{R}_c, R, \vartheta, \varphi, t) = \frac{i}{\hbar} \int_{t_0}^t \mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau \quad ; \quad (72)$$

and the corresponding Born-Oppenheimer electronic potential energy surface (65) reads as

$$V_n(\vec{R}_c, R, \vartheta, \varphi, t) = \mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta(t)) \quad . \quad (73)$$

Equation (73) displays of course an intuitively expected result: *The calculated electronic potentials coincide with those obtained within the conventional Born-Oppenheimer approximation for the time independent static field.*

E. Electronic potential energy surfaces: The ac-field limit

Here we investigate another special case when the electromagnetic field oscillates rapidly and (quasi)periodically in time. Mentioned situation is referred as the ac (alternating current) limit, and is encountered whenever the studied molecule is exposed to an adiabatically switched continuous wave UV-VIS-NIR laser,

$$\vec{E}(\vec{r}, t) = \vec{E}_{\text{ac}}(\vec{r}, \eta(t)) e^{+i\omega_L t/2} + \vec{E}_{\text{ac}}^*(\vec{r}, \eta(t)) e^{-i\omega_L t/2} \quad . \quad (74)$$

Here, symbol ω_L stands for the laser frequency, and the field amplitude $\vec{E}_{\text{ac}}(\vec{r}, \eta(t))$ is allowed to depend very slowly (adiabatically) on a formally introduced switching parameter $\eta(t)$. To avoid confusion, we quote in this context a simple example of a CW-like Gaussian laser pulse $\vec{E}_{\text{ac}}(\vec{r}, \eta(t)) = \vec{E}_0 e^{-\sigma t^2} e^{-i\vec{k}_L \cdot \vec{r}}$ with real parameter $\sigma \rightarrow +0$, $|\vec{k}_L| = \omega_L/c$ and $\vec{E}_0 \cdot \vec{k}_L = 0$. Here the switching parameter $\eta(t)$ can be set to $e^{-\sigma t^2}$ and is then interpreted as an indicator of an instantaneous value of an envelope of the considered light pulse. For the sake of completeness, we note also that the electrostatic potential $\phi(\vec{r}, t)$ has been chosen to be zero in the present example.

Taking into account the property (74) of the field, it is clear that the corresponding Hamiltonian interaction term (43) depends on time only through $e^{\pm i\omega_L t}$ and $\eta(t)$, and can be thus denoted as

$$\begin{aligned} \mathbf{W}_{\text{el}}^{\text{F}}(\vec{R}_c, R, \vartheta, \varphi, \eta(t), t) &\equiv \mathbf{W}_{\text{el}}(\vec{R}_c, R, \vartheta, \varphi, t) = \\ &= - \left[\mathcal{M}(\vartheta, \varphi) \vec{D}_{\text{AB}}^{\text{BF}}(R, \vartheta, \varphi, \vec{r}^N) \right] \cdot \vec{E}_{\text{ac}}(\vec{r}, \eta(t)) e^{+i\omega_L t/2} + \text{c.c.} \end{aligned} \quad (75)$$

If so, the dynamical electronic wavefunctions (45) take an explicit functional form predicted by the adiabatic theorem for the Floquet states [18]. It holds

$$\Phi_n(\vec{r}^N, t; \vec{R}_c, R, \vartheta, \varphi) = \exp\left[-\frac{i}{\hbar} \int_{t_0}^t \mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau\right] \Phi_n^F(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta(t), t) \quad ; \quad (76)$$

where the η -adiabatic Floquet quasienergies and eigenfunctions are defined by a generalized eigenvalue problem

$$\begin{aligned} \left[\mathbf{H}_{\text{el}}(R) + \mathbf{W}_{\text{el}}^F(\vec{R}_c, R, \vartheta, \varphi, \eta, t) - i\hbar (\partial/\partial t) \right] \Phi_n^F(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta, t) = \\ = \mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta) \Phi_n^F(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta, t) \quad . \end{aligned} \quad (77)$$

In above equation (77), the time variable t is treated as an additional dynamical coordinate subjected to a boundary condition

$$\Phi_n^F(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta, t) = \Phi_n^F(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta, t + T) \quad , \quad T = 2\pi/\omega_L \quad ; \quad (78)$$

in accordance with the spirit of the Floquet and (t, t') theories [24]. The Floquet wavefunctions can be expanded using the field free electronic basis set (47) into a sum

$$\Phi_n^F(\vec{r}^N; \vec{R}_c, R, \vartheta, \varphi, \eta, t) = \sum_{n'} \sum_{m=-\infty}^{m=+\infty} C_{mn'}^n(\vec{R}_c, R, \vartheta, \varphi, \eta) \Phi_{n'}^0(\vec{r}^N; R) e^{+im\omega_L t} \quad ; \quad (79)$$

which is reduced just to a single term $\Phi_n^0(\vec{r}^N; R)$ as soon as the field amplitude is turned off. Written mathematically,

$$C_{mn'}^n(\vec{R}_c, R, \vartheta, \varphi, \eta_0) = \delta_{nn'} \delta_{m0} \quad \text{for} \quad \vec{E}_{\text{ac}}(\vec{r}, \eta_0) = \vec{0} \quad . \quad (80)$$

Similarly, also

$$\mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta_0) = \mathcal{E}_n^0 \quad . \quad (81)$$

Strictly speaking, the above outlined formulation of the Floquet theory is physically adequate only in the weak field regime where the associated Floquet states resemble the properties of the bound states. For strong fields, where the field induced ionization phenomenon becomes important, the problem must be addressed within the framework of the non-Hermitian quantum mechanics, with different types of complex scaling transformations being employed to yield *complex* quasienergies [25]. In such a case an imaginary part of the quasienergy corresponds to an inverse lifetime of the associated metastable electronic Floquet state. Further details regarding the Floquet theory can be found in Refs. [24].

Using an adiabatic ansatz (76) we find that the matrix element

$$\langle \Phi_n | (\partial/\partial R) | \Phi_n \rangle_{\vec{r}^N} = -\frac{i}{\hbar} \frac{\partial}{\partial R} \int_{t_0}^t \mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau + \langle \Phi_n^F | (\partial/\partial R) | \Phi_n^F \rangle_{\vec{r}^N} \quad . \quad (82)$$

Analogical relations are valid also for the other matrix elements appearing on right hand sides of equations (59)-(60). Since the system of differential equations (59)-(60) is linear and homogeneous, an appropriate solution should possess the form

$$w_n(\vec{R}_c, R, \vartheta, \varphi, t) = \frac{i}{\hbar} \int_{t_0}^t \mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau + \tilde{w}_n(\vec{R}_c, R, \vartheta, \varphi, t) \quad ; \quad (83)$$

where the quantity $\tilde{w}_n(\vec{R}_c, R, \vartheta, \varphi, t)$ is assumed to satisfy a system of the first order partial differential equations

$$\nabla_{\vec{R}_c} \tilde{w}_n(\vec{R}_c, R, \vartheta, \varphi, t) = -\langle \Phi_n^F | \nabla_{\vec{R}_c} | \Phi_n^F \rangle_{\vec{r}^N} \quad , \quad \partial \tilde{w}_n / \partial R = -\langle \Phi_n^F | (\partial / \partial R) | \Phi_n^F \rangle_{\vec{r}^N} \quad (84)$$

$$\partial \tilde{w}_n / \partial \vartheta = -\langle \Phi_n^F | (\partial / \partial \vartheta) | \Phi_n^F \rangle_{\vec{r}^N} \quad , \quad \partial \tilde{w}_n / \partial \varphi = -\langle \Phi_n^F | (\partial / \partial \varphi) | \Phi_n^F \rangle_{\vec{r}^N} \quad . \quad (85)$$

The question on solvability of Eqs. (84)-(85) does not seem to be less difficult than in the case of Eqs. (59)-(60). For this reason, we prefer to carry out the phase transformation (58) using only the factor

$$w_n(\vec{R}_c, R, \vartheta, \varphi, t) = \frac{i}{\hbar} \int_{t_0}^t \mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta(\tau)) d\tau \quad . \quad (86)$$

Since the function (86) does not represent an exact solution of the problem (59)-(60), the first derivatives of the hamiltonian term $\mathbf{h}_{nn}^{(1)}(t)$ (see Eq. (53) for $n = n'$) are not completely eliminated. Instead, $\mathbf{h}_{nn}^{(1)}(t)$ is transformed into

$$\begin{aligned} \mathbf{h}_{nn}^{(F)}(t) = & -\frac{\hbar^2}{M} \langle \Phi_n^F | \nabla_{\vec{R}_c} | \Phi_n^F \rangle_{\vec{r}^N} \cdot \nabla_{\vec{R}_c} - \frac{\hbar^2}{\mu_{AB}} \langle \Phi_n^F | (\partial / \partial R) | \Phi_n^F \rangle_{\vec{r}^N} \frac{\partial}{\partial R} \\ & - \frac{\hbar^2}{\mu_{AB} R^2} \langle \Phi_n^F | (\partial / \partial \vartheta) | \Phi_n^F \rangle_{\vec{r}^N} \frac{\partial}{\partial \vartheta} - \frac{\hbar^2}{\mu_{AB} R^2 \sin^2 \vartheta} \langle \Phi_n^F | (\partial / \partial \varphi) | \Phi_n^F \rangle_{\vec{r}^N} \frac{\partial}{\partial \varphi} \quad . \end{aligned} \quad (87)$$

Due to presence of the above first derivative term in the effective nuclear hamiltonian, the obtained electronic potential energy surface

$$V_n(\vec{R}_c, R, \vartheta, \varphi, t) = \mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta(t)) \quad (88)$$

accounts only partially for the underlying Born-Oppenheimer nuclear dynamics. Nevertheless, as being explained in the next paragraph, the transformation (58) with the phase factor (86) still proves to be an important step which offers a lot of physical insight.

The nature of the Floquet wavefunctions (79) reveals that all the diagonal matrix elements contained in the formula (87) depend on time solely through the oscillating factors $e^{\pm im\omega_L t}$ (m nonzero integer). Validity of this statement can be most directly demonstrated through an evaluation of the time averages

$$\int_t^{t+T} \langle \Phi_n^F(\tau) | (\partial / \partial \Omega) | \Phi_n^F(\tau) \rangle_{\vec{r}^N} d\tau = 0 \quad , \quad \Omega = (X, Y, Z, R, \vartheta, \varphi) \quad ; \quad (89)$$

by taking advantage of the Feynman-Hellman theory adapted for the Floquet states [18]. Due to presence of the just discussed oscillatory factors, the quantity (88) can be regarded as a physically well justified Born-Oppenheimer potential term in the ac-field limit. This holds true as long as the duration $T = 2\pi/\omega_L$ of one optical cycle remains much smaller than the characteristic timescales of the nuclear motions, so that the oscillating first derivative contribution (87) is irrelevant. On the other hand, the correction (87) becomes increasingly important as ω_L decreases and approaches the dc-field limit. One can see it immediately also from the fact that the above ac-field potential (88) depends on time only through an *envelope* of the light pulse, while the correct dc-field formula (73) is defined in terms of an *instantaneous* field strength and includes thus the field oscillations $e^{\pm i\omega_L t}$. The coming Section IV provides a more explicit comparison of the Born-Oppenheimer potentials in the dc-field and ac-field limits.

IV. DIATOMIC MOLECULE IN AN ELECTROMAGNETIC FIELD: ELECTRONIC POTENTIAL ENERGY SURFACES IN THE WEAK FIELD REGIME

A. Application of the perturbation theory in the dc-field limit

Provided that the used field strength is sufficiently weak, the corresponding Born-Oppenheimer electronic eigenenergies and wavefunctions defined by equation (69) are only slightly different from their field free counterparts. If so, the framework of perturbation theory offers a straightforward method for resolving the mentioned Born-Oppenheimer electronic problem, and leads towards explicit analytic formulas for the field induced corrections of the associated potential energy surfaces, $\mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta) - \mathcal{E}_n^0(R)$. Clearly, the field strength is considered here to be the perturbation expansion parameter, while the solutions of the field free eigenproblem (47) are taken as an unperturbed reference.

Before presenting the details of the perturbation approach, we would like to emphasize that this is not the only practical method for evaluation of the desired dc-field Born-Oppenheimer electronic potential energy surfaces. An alternative possibility is to use direct (*ab initio*) numerical solution of equation (69), which is of course much more demanding from computational point of view, but remains appropriate even in the case of strong dc-fields.

Perturbation expansion for the energy eigenvalue of equation (69) possesses the form

$$\mathcal{E}_n^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta) = \mathcal{E}_n^0(R) + \mathcal{E}_n^{\text{ad},1}(\vec{R}_c, R, \vartheta, \varphi, \eta) + \mathcal{E}_n^{\text{ad},2}(\vec{R}_c, R, \vartheta, \varphi, \eta) + \dots \quad ; \quad (90)$$

where the first order correction

$$\mathcal{E}_n^{\text{ad},1}(\vec{R}_c, R, \vartheta, \varphi, \eta) = \langle \Phi_n^0 | \mathbf{W}_{\text{el}}^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta) | \Phi_n^0 \rangle_{\mathbb{F}^N} \quad ; \quad (91)$$

and the second order term

$$\mathcal{E}_n^{\text{ad},2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = \sum_{n' \neq n} \frac{|\langle \Phi_n^0 | \mathbf{W}_{\text{el}}^{\text{ad}}(\vec{R}_c, R, \vartheta, \varphi, \eta) | \Phi_{n'}^0 \rangle_{\vec{r}^N}|^2}{\mathcal{E}_n^0(R) - \mathcal{E}_{n'}^0(R)} . \quad (92)$$

Substitution of an expression (67) yields consequently more explicit results

$$\mathcal{E}_n^{\text{ad},1}(\vec{R}_c, R, \vartheta, \varphi, \eta) = - \left[\mathcal{M}(\vartheta, \varphi) \langle \Phi_n^0 | \vec{D}_{\mathcal{AB}}^{BF}(R, \vartheta, \varphi, \vec{r}^N) | \Phi_n^0 \rangle_{\vec{r}^N} \right] \cdot \vec{E}_{\text{dc}}(\vec{R}_c, \eta) \quad ; \quad (93)$$

and

$$\mathcal{E}_n^{\text{ad},2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = \sum_{n' \neq n} \frac{\left| \left[\mathcal{M}(\vartheta, \varphi) \langle \Phi_n^0 | e \sum_{j=1}^N \vec{r}_j | \Phi_{n'}^0 \rangle_{\vec{r}^N} \right] \cdot \vec{E}_{\text{dc}}(\vec{R}_c, \eta) \right|^2}{\mathcal{E}_n^0(R) - \mathcal{E}_{n'}^0(R)} . \quad (94)$$

Relation (93) determines of course an energy of an interaction between the molecular permanent dipole moment (associated with given electronic state n) and the total electric field (arising both due to the scalar and the vector potentials). We refer in this context to our discussion of the dipole term $\vec{D}_{\mathcal{AB}}$ carried out at the end of subsection II.C. In passing we note that the just mentioned kind of dipole interaction constitutes a conceptual basis of the traditional rovibrational spectroscopy (we recall that the dc-field limit is appropriate in the microwave and the far infrared spectral domains).

Physical contents of equation (94) becomes apparent after rewriting it into an equivalent fashion

$$\mathcal{E}_n^{\text{ad},2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = -\frac{1}{2} \left[\mathcal{M}(\vartheta, \varphi) \vec{E}_{\text{dc}}^T(\vec{R}_c, \eta) \right] \cdot \vec{\alpha}_n(R) \cdot \left[\mathcal{M}^T(\vartheta, \varphi) \vec{E}_{\text{dc}}(\vec{R}_c, \eta) \right] \quad ; \quad (95)$$

where the symbol

$$\vec{\alpha}_n(R) = 2 \sum_{n' \neq n} \frac{\langle \Phi_n^0 | e \sum_{j=1}^N \vec{r}_j | \Phi_{n'}^0 \rangle_{\vec{r}^N} \langle \Phi_{n'}^0 | e \sum_{j=1}^N \vec{r}_j | \Phi_n^0 \rangle}{\mathcal{E}_{n'}^0(R) - \mathcal{E}_n^0(R)} \quad (96)$$

is recognized as a tensor of static polarizability associated with the n -th electronic state of the \mathcal{AB} molecule. Since the quantity $\vec{\alpha}_n(R)$ is expressed with respect to the body fixed frame defined within subsection II.E, its off-diagonal matrix elements necessarily vanish provided that the relevant electronic state $|\Phi_n^0\rangle$ is of Σ type. (This is the case of the ground electronic states of the vast majority of diatomic molecules.) The situation is a bit more complicated in the case when the electronic states of types Π , Δ , etc. enter into the play. We shall omit all the details for the sake of simplicity, and consider from now on just the Σ type electronic ground state $|\Phi_g^0\rangle$. Symmetry considerations dictate that

$$\alpha_g^{xx}(R) = \alpha_g^{yy}(R) \equiv \alpha_g^\perp(R) \quad , \quad \alpha_g^{zz}(R) \equiv \alpha_g^\parallel(R) \quad , \quad \alpha_g^{xy}(R) = \alpha_g^{xz}(R) = \alpha_g^{yz}(R) = 0 \quad . \quad (97)$$

Moreover, it is clear that the x and y components of the dipole moment matrix element $\langle \Phi_g^0 | \vec{D}_{\mathcal{AB}}^{BF}(R, \vartheta, \varphi, \vec{r}^N) | \Phi_g^0 \rangle_{\vec{r}^N}$ appearing in the first order correction (93) are zero. In order to fully

exploit these useful properties, we assume without any loss of generality that the only nonzero component of the dc electric field is pointing along the space fixed z -axis, i.e.

$$\vec{E}_{\text{dc}}(\vec{R}_c, \eta) = [0, 0, E_{\text{dc}}(\vec{R}_c, \eta)] \quad . \quad (98)$$

Using equations (26), (97) and (98), we simplify the formulas (93) and (95) into

$$\mathcal{E}_g^{\text{ad},1}(\vec{R}_c, R, \vartheta, \varphi, \eta) = -E_{\text{dc}}(\vec{R}_c, \eta) \cos \vartheta \langle \Phi_g^0 | D_{\mathcal{AB}}^{BF,z}(R, \vartheta, \varphi, \vec{r}^N) | \Phi_g^0 \rangle_{\vec{r}^N} \quad ; \quad (99)$$

and

$$\mathcal{E}_g^{\text{ad},2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = -\frac{1}{2} E_{\text{dc}}^2(\vec{R}_c, \eta) \left[\alpha_g^{\parallel}(R) \cos^2 \vartheta + \alpha_g^{\perp}(R) \sin^2 \vartheta \right] \quad . \quad (100)$$

Having derived these two important expressions, we conclude our discussion by writing down the final result for the associated translational/rotational/vibrational Hamiltonian (62) assigned to the ground electronic state diatomic molecule \mathcal{AB} interacting with a weak external dc electromagnetic field. It holds

$$\begin{aligned} \mathbf{h}_g^{\text{eff}}(t) = & -\frac{\hbar^2}{2M} \Delta_{\vec{R}_c} - \frac{\hbar^2}{2\mu_{\mathcal{AB}}} \frac{\partial^2}{\partial R^2} + \frac{\vec{\mathbf{L}}_{\vartheta\varphi}^2}{2\mu_{\mathcal{AB}} R^2} - E_{\text{dc}}(\vec{R}_c, \eta(t)) \cos \vartheta \langle \Phi_g^0 | D_{\mathcal{AB}}^{BF,z}(R, \vartheta, \varphi, \vec{r}^N) | \Phi_g^0 \rangle_{\vec{r}^N} \\ & - \frac{1}{2} E_{\text{dc}}^2(\vec{R}_c, \eta(t)) \left[\alpha_g^{\parallel}(R) \cos^2 \vartheta + \alpha_g^{\perp}(R) \sin^2 \vartheta \right] \quad . \end{aligned} \quad (101)$$

Note that the dc-field enters here through its *instantaneous* time dependent strength $E_{\text{dc}}(\vec{R}_c, \eta(t))$. As being shown in the next subsection, this finding is in a sharp contrast to the situation when an ac-field is present.

B. Application of the perturbation theory in the ac-field limit

The framework of the perturbation theory can be exploited as well in the case of weak ac-fields. Perturbative treatment of the Born-Oppenheimer-Floquet electronic problem (77) leads towards explicit analytic formulas for the field induced corrections of the associated potential energy surfaces, $\mathcal{E}_n^{\text{F}}(\vec{R}_c, R, \vartheta, \varphi, \eta) - \mathcal{E}_n^0(R)$. Similarly as in the above dc-field case, the field strength is considered to be the perturbation expansion parameter, while the solutions of the field free eigenproblem (47) are taken as an unperturbed reference. In passing we note that, since the time variable t is within the Floquet formalism treated as an additional dynamical coordinate, we can still rely here on a (properly modified) time independent perturbation theory. Instead of supplying a more detailed description of such a Floquet type time independent perturbation approach, we refer to [18] and [26] for well elaborated examples.

Similarly as in above subsection IV.A, we would like to emphasize that the perturbation approach is not the only practical method for evaluation of the desired ac-field Born-Oppenheimer electronic

potential energy surfaces. An alternative possibility is to use direct (*ab initio*) numerical solution of the Floquet eigenproblem (77). Such a task is of course much more demanding from the computational point of view, but remains appropriate even in the case of strong ac-fields.

Perturbation expansion for the quasienergy eigenvalue of equation (77) possesses the form

$$\mathcal{E}_n^F(\vec{R}_c, R, \vartheta, \varphi, \eta) = \mathcal{E}_n^0(R) + \mathcal{E}_n^{F,1}(\vec{R}_c, R, \vartheta, \varphi, \eta) + \mathcal{E}_n^{F,2}(\vec{R}_c, R, \vartheta, \varphi, \eta) + \dots \quad ; \quad (102)$$

where the first order correction $\mathcal{E}_n^{F,1}(\vec{R}_c, R, \vartheta, \varphi, \eta)$ vanishes due to time averaging over the ac field oscillations, while the second order term

$$\begin{aligned} \mathcal{E}_n^{F,2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = & \sum_{n' \neq n} \left| \left[\mathcal{M}(\vartheta, \varphi) \langle \Phi_n^0 | e \sum_{j=1}^N \vec{r}_j | \Phi_{n'}^0 \rangle_{\vec{r}^N} \right] \cdot \vec{E}_{ac}^\perp(\vec{R}_c, \eta) / 2 \right|^2 \\ & \times \left\{ \frac{1}{\mathcal{E}_n^0(R) - \mathcal{E}_{n'}^0(R) + \hbar\omega_L} + \frac{1}{\mathcal{E}_n^0(R) - \mathcal{E}_{n'}^0(R) - \hbar\omega_L} \right\} \quad . \end{aligned} \quad (103)$$

Physical contents of equation (103) becomes apparent after rewriting it into an equivalent fashion

$$\mathcal{E}_n^{F,2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = - \left[\mathcal{M}(\vartheta, \varphi) \vec{E}_{ac}^T(\vec{R}_c, \eta) / 2 \right] \cdot \vec{\alpha}_n(R, \omega_L) \cdot \left[\mathcal{M}^T(\vartheta, \varphi) \vec{E}_{ac}(\vec{R}_c, \eta) / 2 \right] \quad ; \quad (104)$$

where the quantity

$$\vec{\alpha}_n(R, \omega_L) = \frac{2}{\hbar} \sum_{n' \neq n} \frac{\langle \Phi_n^0 | e \sum_{j=1}^N \vec{r}_j | \Phi_{n'}^0 \rangle_{\vec{r}^N} \langle \Phi_{n'}^0 | e \sum_{j=1}^N \vec{r}_j | \Phi_n^0 \rangle \omega_{nn'}(R)}{\omega_L^2 - \omega_{nn'}^2(R)} \quad (105)$$

is recognized as a tensor of dynamical (frequency dependent) polarizability associated with the n -th electronic state of the \mathcal{AB} molecule, and an auxiliary symbol

$$\omega_{nn'}(R) = \left[\mathcal{E}_n^0(R) - \mathcal{E}_{n'}^0(R) \right] / \hbar \quad . \quad (106)$$

Since the tensor $\vec{\alpha}_n(R, \omega_L)$ is expressed with respect to the body fixed frame, its off-diagonal matrix elements necessarily vanish provided that we restrict ourselves on the case of the ground electronic state $|\Phi_n^0\rangle \equiv |\Phi_g^0\rangle$ which is assumed to be of Σ type. Symmetry considerations dictate then that

$$\alpha_g^{xx}(R, \omega_L) = \alpha_g^{yy}(R, \omega_L) \equiv \alpha_g^\perp(R, \omega_L) \quad , \quad \alpha_g^{zz}(R, \omega_L) \equiv \alpha_g^\parallel(R, \omega_L) \quad ; \quad (107)$$

and

$$\alpha_g^{xy}(R, \omega_L) = \alpha_g^{xz}(R, \omega_L) = \alpha_g^{yz}(R, \omega_L) = 0 \quad . \quad (108)$$

In order to fully exploit these useful properties, we assume without any loss of generality that the only nonzero component of the considered ac electric field is pointing along the space fixed z -axis, i.e.,

$$\vec{E}_{ac}(\vec{R}_c, \eta) = \left[0, 0, E_{ac}(\vec{R}_c, \eta) \right] \quad . \quad (109)$$

Using Eqs. (26), (107) and (108), we simplify the formula (104) into

$$\mathcal{E}_g^{\text{F},2}(\vec{R}_c, R, \vartheta, \varphi, \eta) = -\frac{1}{4} E_{\text{ac}}^2(\vec{R}_c, \eta) \left[\alpha_g^{\parallel}(R, \omega_L) \cos^2 \vartheta + \alpha_g^{\perp}(R, \omega_L) \sin^2 \vartheta \right] . \quad (110)$$

Note that we encounter here a multiplicative factor (1/4) contrary to the dc-field expression (100) where a factor (1/2) appears instead. Let us write down now the final result for the associated translational/rotational/vibrational Hamiltonian (62) assigned to the ground electronic state diatomic molecule \mathcal{AB} interacting with a weak external ac electromagnetic field. It holds

$$\begin{aligned} \mathbf{h}_g^{\text{eff}}(t) = & -\frac{\hbar^2}{2M} \Delta_{\vec{R}_c} - \frac{\hbar^2}{2\mu_{\mathcal{AB}}} \frac{\partial^2}{\partial R^2} + \frac{\vec{\mathbf{L}}_{\vartheta\varphi}^2}{2\mu_{\mathcal{AB}} R^2} \\ & - \frac{1}{4} E_{\text{ac}}^2(\vec{R}_c, \eta(t)) \left[\alpha_g^{\parallel}(R, \omega_L) \cos^2 \vartheta + \alpha_g^{\perp}(R, \omega_L) \sin^2 \vartheta \right] . \end{aligned} \quad (111)$$

Note that the ac-field enters here solely through its *amplitude* $E_{\text{ac}}(\vec{R}_c, \eta(t))$, while the rapid field oscillations $e^{\pm i\omega_L t}$ do not appear. This behavior is in a sharp contrast to the case of dc-field analyzed within the previous subsection, see equation (101).

Our discussion concludes by pointing out one additional remark. The perturbational analysis performed within this subsection has been based upon the length gauge Hamiltonian defined by formulas (41)-(43). Another option might be to develop a perturbational expansion employing the momentum gauge Hamiltonian (19), of course after having converted it properly into the body fixed frame following similar approach as in above subsections II.D-II.E. Interestingly, the results obtained within the length gauge and the momentum gauge perturbation theory possess somewhat different functional forms. Our calculations reveal that the momentum gauge expression for $\mathcal{E}_n^{\text{F},2}(\vec{R}_c, R, \vartheta, \varphi, \eta)$ is still given by relation (104), with the dynamical polarizability tensor being however redefined as

$$\vec{\alpha}_n(R, \omega_L) = \frac{2}{\hbar} \sum_{n' \neq n} \frac{\langle \Phi_n^0 | e \sum_{j=1}^N \vec{\mathbf{r}}_j | \Phi_n^0 \rangle_{\vec{\mathbf{r}}^N} \langle \Phi_{n'}^0 | e \sum_{j=1}^N \vec{\mathbf{r}}_j | \Phi_n^0 \rangle \omega_{nn'}(R) \frac{\omega_{nn'}^2(R)}{\omega_L^2}}{\omega_L^2 - \omega_{nn'}^2(R)} . \quad (112)$$

The only difference between formulas (105) and (112) consists in the presence of an extra factor $(\omega_{nn'}(R)/\omega_L)^2$. Due to this extra factor, one would be tempted to argue that equations (105) and (112) provide different results for the polarizability. Even a direct numerical calculation using a finite basis set of the field free molecular electronic states $\{|\Phi_{n'}^0\rangle\}$ shows that the predictions of the formulas (105) and (112) are different. Especially pronounced discrepancies are found in the case when ω_L is far off resonant from any electronic transition $|\Phi_n^0\rangle \rightarrow |\Phi_{n'}^0\rangle$. Mentioned observations might seem to indicate inconsistencies, since the passage from the momentum gauge to the length gauge is facilitated through an unitary transformation, and the quantum mechanical perturbation theory is known to be gauge invariant. A detailed theoretical analysis of the above sketched problem is postponed into another paper [27]. Here we just state without proof that both expressions (105) and (112) turn out to be identical, *provided that one properly accounts for a complete set of all the electronic states*,

including also the highly excited electronic continuum. Use of a truncated basis set in equation (112) is not always justified and can provide an absolutely misleading outcome. This example should serve as a warning against an incautious use of an incomplete electronic basis set (e.g. within the widely considered two level approximation) when studying the field induced atomic/molecular properties in the momentum gauge.

V. CONCLUDING REMARKS

In the present paper, we have studied general problem of the translational/rotational/vibrational/electronic dynamics of a diatomic molecule exposed to an interaction with an arbitrary external electromagnetic field. We have derived an appropriate body fixed frame Hamiltonian (41), and introduced the concept of the time dependent Born-Oppenheimer approximation. An interesting open question on general existence of the time dependent Born-Oppenheimer electronic potential energy surfaces has been raised. Finally, we have derived an effective translational/rotational/vibrational Hamiltonian (101) resp. (111) of a ground electronic state diatomic molecule in a weak dc/ac field. Our entire derivation is based upon the first quantum mechanical principles and well defined approximations.

The theory developed in this paper is believed to be of importance for a variety of specific applications, like e.g. alignment/orientation of molecules by lasers, trapping of ultracold molecules in optical lattices, molecular optics and interferometry, rovibrational spectroscopy of molecules in the presence of intense laser light, or harmonic generation. Moreover, the above outlined approach can be extended in a relatively straightforward manner to the most general case of a polyatomic molecule interacting with laser light.

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